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(54) Cross-linkable thixotropic wood adhesive gel

(57) A cross-linkable water-based wood adhesive comprised of a critical mixture of from 0.10 to 0.75 by weight of a water-soluble, high-viscosity thickening agent polymer such as hydroxyethylcellulose, 0.05 - 0.40% by weight of a defoamer to dissipate foam quickly during manufacture, 25.00 to 45.00% by weight of solids of a self-cross-linking polyvinyl acetate polymer (treated with N-methylolacrylamide) dispersed in water, the polymer having a molecular weight of about 30,000 to about 300,000, 1.00 - 3.00% by weight of a plasticizer/coalescing agent such as 2,2,4-trimethyl-1,3 pentanediol monoisobutyrate, 0.50 to 1.00% of an acidic catalyst, such as aluminum chloride, 4.00 to 12% by weight of fine particle-size wood fibers (soft or hard wood fibers or a mixture of both) and 0.10% by weight of a preservative. The viscosity of this adhesive gel will "break-down" when its container, e.g. a squeeze-bottle or flexible tube is finger-pressed resulting in a sufficiently low viscosity to allow for easy extrusion from the small orifices, approximately 0.10 inch diameter or a rectangular slit opening such as approximately 1/16" wide by 5/16" long of the adhesive application tips attached to such squeeze-bottles and flexible tubes. When pressure is released after the desired amount of adhesive flows out of the container, the adhesive quickly reverts very closely to its original gel state so that it will not "run" on vertical surfaces nor "spill" when used as a general purpose wood adhesive. This adhesive has sufficient wet tack to hold two pieces of wood together while still allowing repositioning of the pieces of wood before drying. In addition, since this product contains real wood fibers, its dry film is stainable and easy to sand.

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spindle, the viscosity is about 10,000 cps to 50,000 cps, preferably about 14,000 cps to 35,000 cps, most preferably 14,500 to 25,500 cps, provided that the thixotropic index is within the ranges set forth herein.

Thixotropic index as used herein should be about 1.5 to 7, preferably 2 to 5 and is determined by dividing the viscosity of the gel at 2 RPM by the viscosity of the gel at 20 RPM at 25 • C as measured with an RVF Brookfield viscometer using a number 6 spindle.

Polyvinyl Acetate

The adhesive agent used in this invention is principally polyvinyl acetate polymer.

Polyvinyl acetate polymer is readily commercially available as an aqueous dispersion or emulsion and can be readily made by polymerization techniques known in the art using free radical or redox catalysts such as taught in U.S. Patent 4,085,074 and its Reissue Patent 30,576, the entire disclosures of which are herein incorporated by reference in their entireties.

Preferably the polyvinyl acetate polymer of this invention is copolymerized with an N-alkylol derivative of an amide of an alpha, beta-unsaturated carboxylic acid, such as N-methylol acrylamide.

The composition usually contains about 25% to about 45% of this cross-linkable polyvinyl acetate polymer.

The polyvinyl acetate polymer has a molecular weight (MW) of about 30,000 to about 300,000, preferably 50,000 to 200,000. Although the solids content and viscosity of the emulsion can vary typical total solids content can be about 40% to about 65% by weight of the polyvinyl acetate polymer emulsion. A typical physical properties and general information of one type of polyvinyl acetate emulsion used by us are found in Table I:

Table I

Solids[1]	50.0 to 52.5%
Viscosity[2]	6,000 to 10,000 cps
pH	4.0 to 5.0
Weight/gallon	9.1 lbs.
Residual Monomer	0.09 Max. %
Appearance	Milky White Liquid
Particle Size Average	Less than 1 Microns
Surfactant System	Nonionic
Surface Tension[3]	46 Dynes/cm
Mechanical Stability[4]	Excellent
Freeze-Thaw Stability	Do Not Freeze
Other Information	Borax Incompatible
Typical Polymer Film Properties	
Film	Stiff, Cloudy
Tg[5]	+ 40 degrees C

[1]Ohaus Moisture Balance
[2]Brookfield Viscometer Model RVF, at 20 RPM at 25 • C.
[3]P.B. Tensiometer LG-60/40 E/W Dilution with Water
[4]Does not break after 15 minutes at high speed in Waring Blender
[5]Differential thermal analysis

The emulsion of Table I includes polyvinyl alcohol. However, if the polyvinyl acetate emulsions are initially prepared from polyvinyl acetate polymer, stabilizers, such as polyvinyl alcohol (or partially hydrolyzed polyvinyl alcohol) can be introduced into the polyvinyl acetate emulsion in amounts sufficient to achieve stabilization of the emulsion.

Thickening Agent

The adhesive gel of the present invention preferably comprises a thickening agent. The present inventors have found that a non-ionic, water soluble polymer of high viscosity is particularly suitable as a thick ning agent, although other water soluble thickening agents can be used without departing from the

wood, e.g. pine, or mixtures of hardwood and soft wood. In addition to imparting sandability and stainability to the dried film, the fiber filler permits the attainment of higher viscosity in the composition and a tougher adhesive film during the early stages of cure. Thus, the adhesive film is tougher than the same composition without the fiber filler during the early stages of cure. In other words, the film is "softer" during cure of compositions which do not contain the fiber filler.

The preferred wood fiber filler is in finely divided particle form known as wood flour which generally has a particle size (U.S. Standard Sieve services) of less than about 10 mesh (2000 microns), and preferably less than 20 mesh (850 microns). Although both hard wood, e.g. maple, and soft wood, e.g. pine, are suitable, the preferred wood flour is that of a soft wood, e.g. pine.

Water

The total quantity of water includes water from the polyvinyl acetate emulsion used in making the adhesive, if the polyvinyl acetate is incorporated in the adhesive as an aqueous emulsion. The total quantity of water can also include additional quantities of water added in the preparation of the adhesive as well as that carried by the component ingredients. The quantity of water will generally vary from about 40% to 85% by weight of the adhesive, preferably 45% to 75% and particularly 50% to 65%.

Preservative

If the adhesive gel of the present invention is to be packaged, it is preferably to add a preservative. Particularly preferred is a microbicide for the control of bacteria and fungi.

Suitable materials are readily commercially available, such as the industrial preservatives sold under the trademark KATHON®LX and LX 1.5% from Rohm and Haas Company. The active ingredients in such preservatives are 5-chlor-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one.

Other materials, such as 2-n-octyl-4-isothiazolin-3-one are sold under the trademark SKANE® M-8 by Rohm and Haas Company as a mildewcide can also be included in the composition.

When used the preservative (or combination of preservatives) are each incorporated in an amount preferably not exceeding 0.10% by weight of the composition.

The Package

The package for the thixotropic adhesive gel of the present invention can be a conventional, flexible, squeeze bottle or collapsible tube.

Such packages are generally well known in the art and made of various materials such as plastics, e.g. low density polyethylene. The collapsible tube may even be made of a malleable metal. However, in such a case the contents of the package will not be visible. Thus, to impart the ability to see the contents of the package it may be desirable to make the package of a translucent or transparent plastic material. Illustratively, a squeeze bottle, such as one having a capacity of 4 fluid ounces, is the plastic squeeze bottle used for ELMER'S SCHOOL GLUE of Borden, Inc. Such dispensers are shown in our above-mentioned U.S. Patent 5,284,897, which has been heretofore incorporated by reference, in its entirety.

The dispenser cap orifice has a size which has been designed to allow a steady stream of the contents of the container to be dispensed upon mere finger pressure being applied to the container walls. As discussed herein, the relatively high viscosity of the adhesive gel as packaged in the container breaks down due to its thixotropic properties to allow the gel to steadily flow through the orifice upon mere finger pressure. Suitable orifice openings are approximately 0.06 to 0.15 inches in diameter, preferably 0.10 inch in diameter. Alternatively, the use of a rectangular slit of approximately one sixteenth of an inch wide by five-sixteenths of an inch long is appropriate.

In order that those skilled in the art may more fully understand the invention presented herein, the following examples and comparative examples are set forth. All parts and percentages in the examples and comparative examples, as well as elsewhere in this application, are stated by weight, unless otherwise specifically stated. The viscosity measurements referred to herein are by use of an RVF Brookfield viscometer with a number 6 spindle at 25 • C unless otherwise specifically stated. The term "Low Shear" refers to viscosity measurements at 2 RPM whereas "High Shear" refers to viscosity measurements taken at 20 RPM.

Water-resistance tests were performed in the following manner:

Each of the samples tested was drawn down with a No. 34 wire-wrapped rod to about a two inch width band of adhesive film on a glass plate. The drawn down adhesives were permitted to dry by standing at

Example 2

A composition D was made according to the following formula:

	% by Weight
Water	18.98
KELZAN	0.25
Colloids-581	0.25
PD-312L	70.00
TEXANOL	1.50
KATHON LX 1.5%	0.10
SKANE M8	0.10
Pine flour 14020	6.12
	97.30*

*2.7% of $AlCl_3$ was omitted because it reacts with xanthan gum. Instead, 6 drops H_3PO_4 was added to reduce the pH to 2.8-3.0.

Composition D cross-linked and had good water resistance, but not as good as the water resistance of the formulations using $AlCl_3$ and HEC of Example 5.

Comparative Example 2

A composition E, identical to composition D was formulated except that no such catalyst was added. The composition did not cross-link and gave poor water resistance properties.

Comparative Example 2-A

A composition F was made of a blend of 100 grams of composition D and an equal amount of the composition of Example 1 of our U.S. Patent 5,306,749. 8 drops of H_3PO_4 were added to reduce the pH to 2.8 to 3.0. Results were similar to that of composition C of Comparative Example 1-A.

Example 3

Further composition G was made which includes some partially hydrolyzed polyvinyl alcohol (VINOL-840) to study its affect upon the adhesive gel according to the following formulation:

	% by Weight
Water	17.98
VINOL-840	1.00
KELZAN	0.25
Colloids-581	0.25
PD-312L	70.00
TEXANOL	1.50
KATHON LX 1.5%	0.10
SKANE M8	0.10
Pine flour	6.12
	97.30*

*2.7% $AlCl_3$ was omitted for the reasons noted in Examples 1-2. Instead, 6 drops H_3PO_4 were added to reduce the pH to 2.8-3.0.

A cross-linkable adhesive gel was obtained which had good water resistance but not as good as the water resistance of the preferred formulations using $AlCl_3$ and HEC shown in Example 5.

			% by Weight	
			J	JA
(1) PD-312 L Emulsion			75.82	73.48
(2) TEXANOL			1.66	1.60
(3) Aluminum Chloride (28% Sol. in Water)			2.89	2.80
(4) Colloids 581			.10	.10
(5) KATHON LX 1.5%			.10	.10
(6) SKANE-M8			.10	.10
(7) Pine Flour 14020			6.50	6.29
(8) NATROSOL 250 HHXR (3% Sol. in Water)			10.33	10.00
(9) Water (Adjusting)			2.50	5.50
			100.00	100.00
Viscosity/Brookfield RVF #6 Sp. @ 25 • C				
	Initial	2 RPM 20 RPM Thixotropic Index	45,000 23,500 1.9	32,500 16,500 1.9
	Overnight	2 RPM 20 RPM Thixotropic Index	45,000 22,500 2.0	30,000 16,000 1.87
	After 1 week	2 RPM 20 RPM Thixotropic Index	60,000 20,500 2.9	30,000 14,500 2.0
	After 1 Month	2 RPM 20 RPM Thixotropic Index	85,000 21,000 4.0	60,000 15,000 4.0
pH			2.8	2.9
% Solids			49	47
Wt./Gal. (lbs.)			9.2	9.1
Water-Resistance			Excellent	Excellent
Both compositions J and JA showed excellent water resistance with a higher degree of resistance to fracturing of their films under the drop after two hours.				

The manufacturing procedure for composition J and JA is as follows:

1. In a clean dry tank add (1). Start mixer on low speed and add (2), (3) –wear safety glasses and gloves and avoid splashing, (4), (5) and (6), mixing thoroughly after addition of each item.
2. Increase mixing speed to moderate and add (7) in increments allowing wood fibers to mix thoroughly after each addition.
3. Add (8) in increments and continue to mix until the batch is homogeneous. Remove a sample for quality control check.
4. After quality control check, adjust viscosity with (9) as necessary. Composition J and JA can be packaged in polyethylene squeeze bottles.

Having now fully described the invention, it will be apparent to those skilled in the art that many changes and modifications can be made thereto without departing from the spirit of the invention as set forth herein.

Claims

1. A thixotropic adhesive gel comprising a self-cross-linking polyvinyl acetate polymer and a cellulose fiber filler.

2. The adhesive gel of claim 1 wherein the self-cross-linking polyvinyl acetate polymer is copolymerized with N-methylol acrylamide.

3. The adhesive gel of claim 1 further comprising a water soluble high viscosity thickener.

4. The adhesive gel of claim 1 wherein the polyvinyl acetate polymer is cross-linked through the action of an acidic metal cross-linking catalyst.

5. The thixotropic adhesive gel of claim 1 further comprising a plasticizer/coalescing agent.

6. The adhesive gel of claim 1 further comprising a defoamer.

7. The adhesive gel of claim 1 further comprising a preservative.

8. A package containing a thixotropic self-cross-linkable adhesive gel, said package comprising a sealed flexible container having an orifice opening, said thixotropic adhesive gel comprising a self-cross-linking polyvinyl acetate polymer, said adhesive gel having a sufficiently high viscosity as to not flow through said orifice at atmospheric pressure but flowable through said orifice under finger pressure applied to said container, said adhesive gel being capable of reverting to substantially its original viscosity upon exiting said orifice, such that it will not run on vertical surfaces nor spill from its package.

9. The package of claim 8 wherein said adhesive gel comprises:
   (A) polyvinyl acetate copolymerized with N-methylol acrylamide; and
   (B) a cellulosic fiber filler.

10. The package of claim 8 which contains a thixotropic adhesive gel consisting essentially of:
   (A) 0.10 to 0.75% by weight of a water soluble, high viscosity thickening agent polymer;
   (B) 0.05 to 0.40% by weight of a defoamer;
   (C) 25 to 45% by weight (solids) of a self-cross-linking polyvinyl acetate polymer dispersed in water;
   (D) 0.5 to 10.0% by weight of a plasticizer/coalescing agent;
   (E) 0.50 to 1.00% by weight of an acidic catalyst;
   (F) 4.00 to 12% by weight of a cellulosic fiber filler; Hdzfasern
   (G) 0.10% by weight of a preservative, and
   (H) optionally additional water to total 100%.

11. The package of claim 10 wherein the high viscosity thickening agent copolymer comprises hydroxyethylcellulose; the cellulosic fiber filler comprises fine wood fibers and the acidic catalyst comprises aluminum chloride.

12. The package of claim 11 when the self-cross-linking vinyl acetate polymer comprises a vinyl acetate copolymerized with N-methylol acrylamide, dispersed in water, said polymer having a molecular weight from about 30,000 to about 300,000.

13. The package of claim 12 wherein the plasticizer and coalescing agent is 2,2,4-trimethyl-1,3 pentanediol monoisobutyrate.

14. A process for preparing an aqueous self-cross-linking adhesive gel which comprises mixing, by weight:
   (A) from 0.10 to 0.75% of a water-soluble, high viscosity thickening agent;
   (B) from 0.05 to 0.40% of a defoamer;

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EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT

EP 95300549.3

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.6)
X	DATABASE WPIL, no. 82-67208, DERWENT PUBLICATIONS LTD., London; & JP-A-57 108 175 (NIPPON SYNTH CHEM IND.) * Abstract * --	1	C 09 J 131/04 C 09 J 11/00
A	DATABASE WPIL, no. 93-299 837, DERWENT PUBLICATIONS, London; & JP-A-05 214 306 (NIPPON SYNTH CHEM IND.) * Abstract * ----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.6)

C 09 J 131/00
C 09 J 11/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	18-09-1995	PAMMINGER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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